



**Towards cluster-assembled materials of true monodispersity in size and chemical environment:
Synthesis, Dynamics and Activity**

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Final Report**

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14. ABSTRACT This project by the Physical Chemistry group at TUM focused on the surface dynamics of size-selected clusters, studied with local Scanning Probe Microscopy methods. To this purpose, special fast STM techniques for the detection of the cluster dynamics, by imaging (FastSTM) and by tracking (cluster Tracking), have been implemented that were never used before for the study of size-selected clusters. This implementation can now routinely be used and has been applied for first investigations of surface reactions and cluster diffusion. In parallel to these local, microscopy studies, integral studies at ambient pressures have been performed to obtain a systematic insight into cluster ripening control. All the results obtained so far are given in the following summary and are listed in detail at the end (point P1 to P10).					
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Final report

Towards cluster-assembled materials of true monodispersity in size and chemical environment:
Synthesis, Dynamics and Activity

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This project by the Physical Chemistry group at TUM focused on the surface dynamics of size-selected clusters, studied with local Scanning Probe Microscopy methods. To this purpose, special fast STM techniques for the detection of the cluster dynamics, by imaging (**FastSTM**) and by tracking (cluster **Tracking**), have been implemented that were never used before for the study of size-selected clusters. This implementation can now routinely be used and has been applied for first investigations of surface reactions and cluster diffusion. In parallel to these local, microscopy studies, integral studies at ambient pressures have been performed to obtain a systematic insight into cluster ripening control. All the results obtained so far are given in the following summary and are listed in detail at the end (point P1 to P10).

In order to get maximum control on the cluster dynamics to be investigated, **truly monodisperse metal clusters on highly ordered Moiré films of supported graphene and hexagonal boron nitride** were studied. As we could demonstrate, the high order of these cluster-assembled materials allowed for a study of cluster diffusion and ripening in unprecedented detail. Indeed, the strict size control of the clusters made the identification of different isomer classes by their height feasible. Isomer interconversion and, for the first time, **isomer-dependent diffusion** were observed in the local diffusion dynamics, as followed by STM time series (**P1**) [1]. These studies (complemented by theoretical calculations of the Landman group) revealed the unique potential of the Moiré films to explore surfaces with **periodical wettability**, i.e. with specific binding sites that are separated by non-binding areas, similar to the cluster immobilization at defects on non-wettable oxide supports. The ripening on these periodically wettable surfaces has been studied by static, highly resolved STM measurements of **height distribution functions**, over large ensembles of clusters and by applying specific image analysis algorithms (**P2**). For Pd clusters it could be shown that on appropriate Moiré substrates, in particular h-BN-Moiré films on Rh(111), Smoluchowski (SR) as well as Ostwald ripening (OR) could be suppressed up to 550 K, which corresponds to the Hüttig temperature (30% of the metal melting temperature), a rule-of-thumb upper limit for atom detachment from nanoparticles on weakly binding substrates [2]. A detailed analysis of ripening clusters on g/Rh(111) reveals an apparent **adsorption site crossover**, when the clusters exceed a critical size, due to the concomitant adhesion to two anchoring sites of the periodically wettable substrate (**P3**). Interestingly, this binding configuration and cluster shape cannot be reached by artificial OR, induced by dosing monomers on the cluster-covered surface.

While these STM ripening studies regarded the thermodynamics of cluster stability, concepts of **kinetic stabilization** have been studied as well, under harsh reaction conditions (**P4**): In an ambient study together with the Langhammer group it could be demonstrated that monodisperse cluster samples indeed survive severe Ostwald ripening conditions much better than their size-unselected counterparts, due to equalization of the mutual atom exchange flux [3].

We are currently reviewing these stabilization concepts in an invited article (**P5**). The ability to improve the **cluster stabilization limit** is fundamental for reaction studies of size-selected clusters at elevated temperatures. As first integral measurements in this temperature window we performed thermal desorption studies on the ethene hydrogenation on Pd₁₉/h-BN/Rh(111), which demonstrat-

ed that the formation of ethane can indeed be detected, even at the very low cluster coverages applied to avoid dimer formation upon cluster deposition (**P6**).

As a prerequisite for the growth of extended and highly ordered graphene-Moiré films, and as a touchstone for the study of surface reaction dynamics with FastSTM, the film formation starting from the catalytic decomposition of ethene has been investigated in detail by variable temperature STM (**P7**). The complete **surface organochemical pathway** could be revealed and polyaryl intermediates with precise morphologies could be selectively obtained by appropriate temperature control, namely 1D-PAH chains and size-selective 2D-PAH clusters consisting of 24 carbon atoms (collaboration with Schaub and Landman group [4]). One crucial intermediate in the Diels Alder-like surface polymerization is a C_4 species that forms by ethene dimerization. Its diffusion is too fast to be resolved at the elevated temperatures required to activate the polymerization, but we could resolve it by applying the FastSTM setup (**P8**). Applying the FastSTM method in a conventional STM requires the appropriate choice of scanning frequencies. We have now published this approach and got the European and US patent granted (**P9**).

The very highlight of the obtained results is however the **Cluster Tracking approach (P10)**: we could trace a 2-layer Pd_{12} cluster on Moiré-graphene (highly diffusing at RT, as shown in P1) over 30 min with a time resolution of 10 ms, over distances up to 60 nm with atomic resolution, while applying a tunneling current of only 1 pA. These first encouraging results indicate that we have now indeed **gained access to the atomic processes that make a whole cluster diffuse**.

In summary, the project "Towards cluster-assembled materials of true monodispersity in size and chemical environment" has been successful from the technological as well as from the scientific point of view.

While we have learned a lot on thermodynamic and kinetic cluster size control on periodically wettable surfaces, new questions came up concerning the link between diffusivity and structural fluctuations that we can only investigate now, with the just implemented instrumentation. We have not reached so far all the proposed goals – the influence of adsorbates and reactions on cluster diffusion have only partially been studied, by measurements under ambient conditions, but yet without an insight into the dynamics at the atomic scale.

In the following, **key findings** and relevant achievements are listed in detail. For the published and submitted work we give only a short summary.

P1. Cluster diffusion: Isomer-dependent diffusion

Status: published

Wang, Bo; Yoon, Bokwon; Koenig, Michael; Fukamori, Yves; Esch, Friedrich; Heiz, Ueli; Landman, Uzi: *Size-Selected Monodisperse Nanoclusters on Supported Graphene: Bonding, Isomerism, and Mobility*. Nano Lett. **12**, 2012, 5907-5912.

Soft-landing of size-selected Pd_N ($N \leq 20$) nanoclusters on a Moiré-patterned surface of graphene adsorbed on Ru(0001) leads to controlled formation of a truly monodisperse cluster-assembled material. Combined scanning tunneling microscopy and first-principles calculations allow identification of selective adsorption sites, characterization of size-dependent cluster isomers, and exploration of interconversion processes between isomeric forms that manifestly influence cluster surface mobility. These surface-assembled cluster superstructures can be employed in nanocatalytic applications, as well as in fundamental investigations of physical factors controlling bonding, structure, isomerism, and surface mobilities of surface-supported clusters.

P2. Cluster ripening: Stabilization on periodically wettable surfaces

Status: published

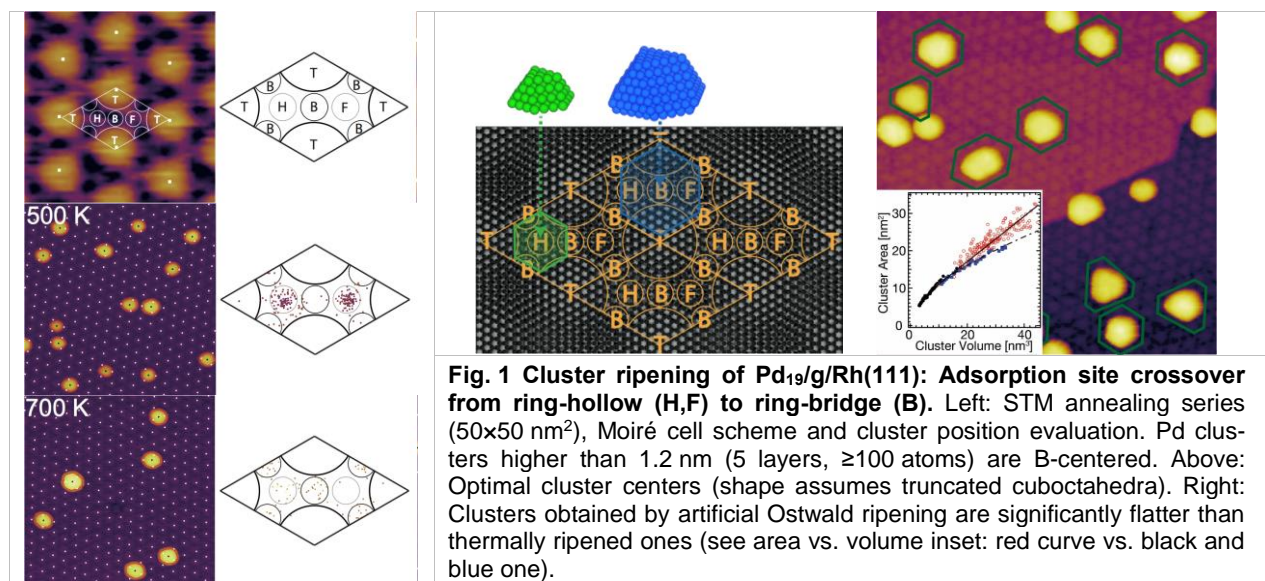
Fukamori, Yves; König, Michael; Yoon, Bokwon; Wang, Bo; Esch, Friedrich; Heiz, Ueli; Landman, Uzi: *Fundamental Insight into the Substrate-Dependent Ripening of Monodisperse Clusters*. ChemCatChem **11**, 2013, 3330-3341.

The sintering properties of cluster-assembled materials can be influenced by tuning the interactions between particle and substrate. To explore the fundamental factors that control cluster-ripening mechanisms, we deposited truly monodisperse Pd clusters onto three different model catalysts: bare Rh(111), graphene-Moiré films that were grown on Rh(111) and Ru(0001), and a hexagonal boron-nitride film that was grown on Rh(111). The evolution of particle size and density was tracked by high-resolution scanning tunneling microscopy. The principal microscopic mechanisms that govern the ripening processes on each of these three substrates have been determined from thorough analyses of the cluster heights and size distributions. The ripening mechanisms were related to the distinct cluster-adsorption and atom-detachment energies that were obtained from first-principle calculations.

P3. Cluster ripening: Adsorption site crossover via cluster diffusion

Status: not yet published

Pd-clusters on Rh(111)-supported Moiré-graphene experience a peculiar adsorption site crossover upon thermal ripening: clusters consisting of more than around 100 atoms start to be centered on positions just in between the two wettable binding sites where smaller clusters are bound most strongly – by this shift the overall adsorption strength is optimized. This behavior is also found on similar graphene films on Ru(0001), even if small clusters initially adsorb only on one of the wettable sites. On similar boron nitride films, however, where the cluster adsorption energy is much stronger modulated in a way that the cluster diffusion (Smoluchowski ripening) is strongly suppressed, no crossover is observed. That the observed sintering is indeed dominated by Smoluchowski ripening, can be derived from the cluster shapes: When inducing the cluster growth alternatively by dosing Pd atoms (“artificial Ostwald ripening”), much flatter clusters result. They grow proportionally to the surrounding capture zone (that can be determined by a Voronoi analysis), as expected for a process in which a diffusing atom gas is collected.



P4. Cluster ripening: Inhibiting Ostwald ripening by size selection

Status: published

Wettergren, Kristina; Schweinberger, Florian F.; Deiana, Davide; Ridge, Claron J; Crampton, Andrew S; Rötzer, Marian; Hansen, Thomas W.; Zhdanov, Vladimir P; Heiz, Ueli; Langhammer, Christoph: *High Sintering Resistance of Size-Selected Platinum Cluster Catalysts by Suppressed Ostwald Ripening*. Nano Letters **14**, 2014, 5803-5809.

Zhdanov, Vladimir P.; Schweinberger, Florian F.; Heiz, Ueli; Langhammer, Christoph: *Ostwald ripening of supported Pt nanoclusters with initial size-selected distributions*. Chem. Phys. Lett. **631–632** (2015) 21–25.

In these two studies, we demonstrate by means of combining noninvasive in situ indirect nano-plasmonic sensing and ex situ scanning transmission electron microscopy that monomodal size-selected platinum cluster catalysts on different supports exhibit remarkable intrinsic sintering resistance even under reaction conditions. The observed stability is related to suppression of Ostwald ripening by elimination of its main driving force via size-selection. The experimental results can be reproduced by corresponding kinetic Monte Carlo simulations that track systematically the role of the initial size distribution. These studies were the first systematic experimental investigations of sintering processes in nanoparticle systems with an initially perfectly monomodal size distribution under ambient conditions.

P5. Derivation of a concept for cluster stabilization

Status: not yet published

Catalysis based on matter in small dimensions has always to cope with stability issues. Due to the high surface area, cluster-assembled materials are energetically frustrated and tend intrinsically to ripen. This review presents a general blueprint for the rational design of sintering resistant catalyst and for efficient experimental strategies to determine sintering mechanisms. While Smoluchowski ripening is reduced by maximizing the cluster binding to the substrate, the kinetic and thermodynamic driving forces that lead to Ostwald ripening are more difficult to handle. The cluster binding to the substrate has to be optimized while minimizing the binding of diffusing individual atoms between the clusters in order to minimize atom detachment and the exchange of matter between the clusters. These thermodynamic driving forces can be controlled by the use of surfaces with laterally modulated wettability, i.e. **periodically wettable surfaces**. This concept is a general one and extends from Moiré-structured graphene films to a wealth of oxide substrates, where defects act as distributed binding sites, whereas stoichiometric areas in between block the diffusing monomers.

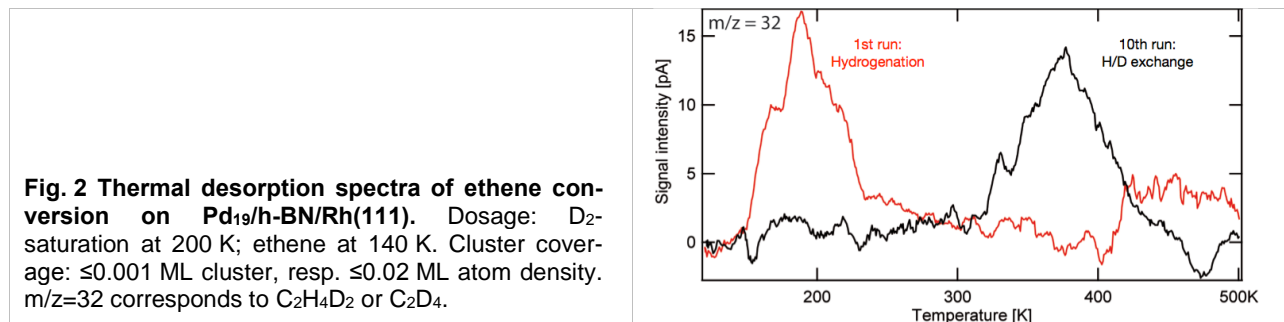
At high temperatures around the so-called Hüttig temperature, however, low coordinated atoms start to detach anyhow from the clusters and Ostwald ripening takes place. Here, **size control** can overcome the kinetic driving forces. Monomodal cluster distributions miss the differences in excess surface energy; every cluster experiences hence similar in- and outgoing fluxes of matter. Even if fluctuations will at the end destroy the monodispersity, ripening can strongly be suppressed and a temperature window opened where clusters transiently survive above the Hüttig temperature.

P6. Cluster reactivity: Ethene hydrogenation by supported, size-selected Pd clusters

Status: ongoing research

The strict size control that can be reached in our cluster deposition comes at the price of low cluster coverages (in order to avoid dimerization). While this is an advantage for Tracking measurements, integral measurements on the cluster reactivity, crucial for the insight into the cluster catalytic activity, require, as a consequence, extremely high sensitivity and low background signals. We implemented and optimized a thermal desorption setup (Feulner cone) in order to hierarchically scan ongoing surface reactions along their spectrum of activation energies. The reaction of coadsorbed deuterium and ethene could be investigated on graphene-supported Pd₁₉ clusters with only 0.1% ML cluster coverage. Besides ethene-coordination to the clusters, we observe that they catalyze

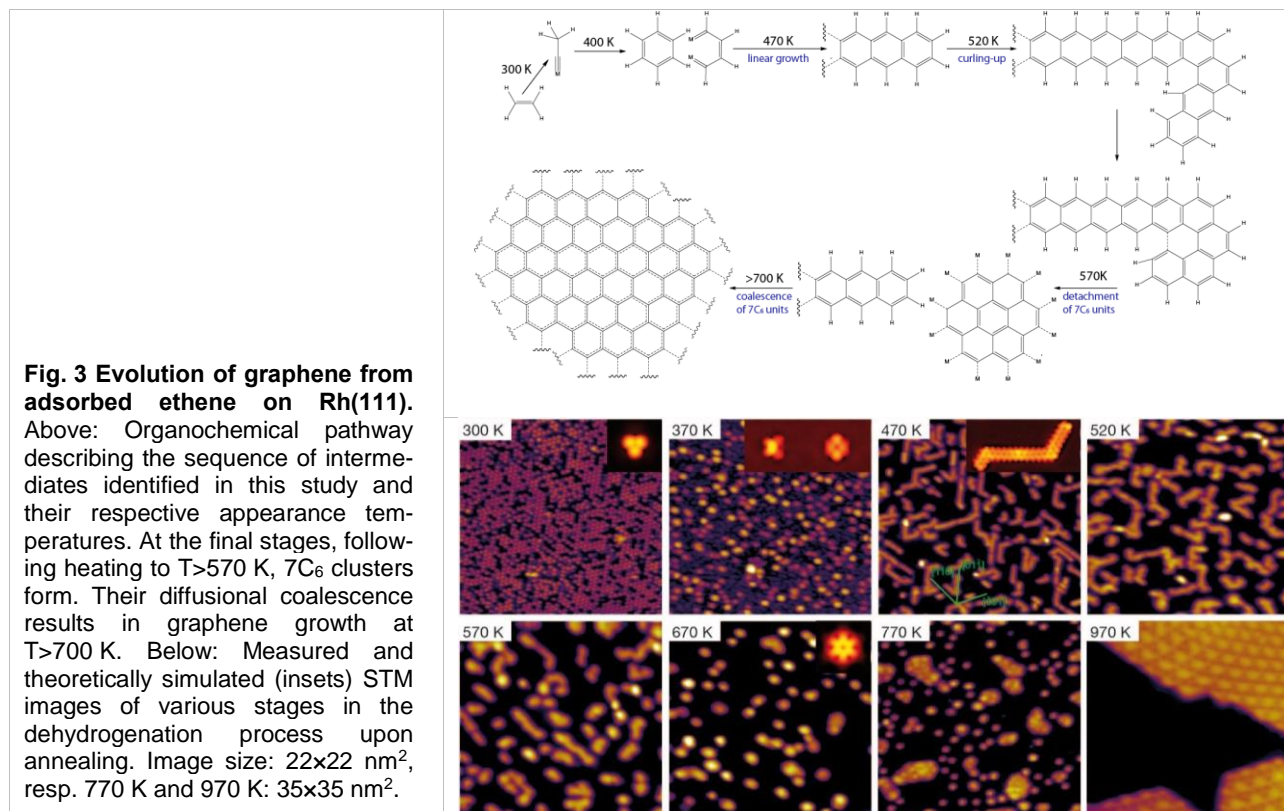
first the hydrogenation (at temperatures 80 K below that for an extended Pd surface [5]), while later the H/D exchange prevails. It will be interesting to see whether this relates to formation of a carbon layer and how this behavior changes when applying high pressures.



P7. Graphene growth: Observing a surface organochemical reaction pathway

Status: not yet published

Diverse technologies, from catalyst coking to graphene synthesis, entail hydrocarbon dehydrogenation and condensation reactions on metals, and assembly into carbon overlayers. Imperative to gaining control over these processes, through thermal steering of the formation of polyaryl intermediates and the controlled prevention of coking, is the exploration and elucidation of the detailed reaction scheme that starts with adsorbed hydrocarbons and culminates with the formation of extended graphene. Here we use Scanning Tunneling Microscopy and Spectroscopy techniques in



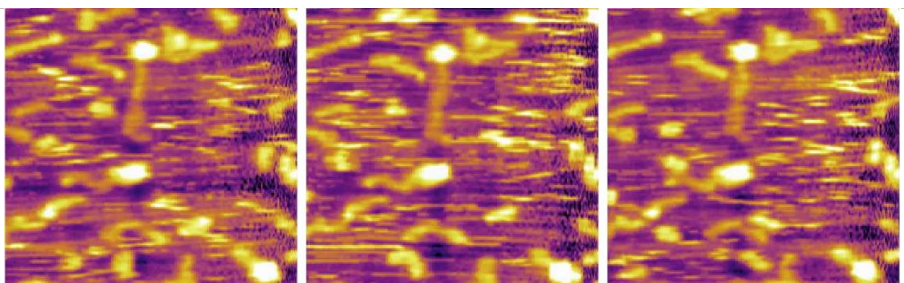
combination with theoretical simulations to uncover the hierarchy of pathways and intermediates underlying the catalyzed evolution of ethene adsorbed on Rh(111) to form graphene. These investigations allow formulation of a reaction scheme whereby, upon heating, adsorbed ethene evolves via coupling reactions to form segmented one-dimensional polyaromatic hydrocarbons (1D-PAH). Further heating leads to dimensionality crossover (1D→2D) and dynamic restructuring processes at the PAH chain ends, with subsequent activated detachment of 24-carbon-atom dehydrogenated-coronene-like clusters. Rate-limiting diffusional coalescence of these dynamically self-evolved precursors culminates (≤ 1000 K) in condensation into graphene of high structural perfection.

P8. FastSTM: Implementation and first results

Status: implementation accomplished, ongoing research

In collaboration with the ELETTRA electronics workshop and the IOM-CNR TASC "Structure and Reactivity" laboratory at Trieste, the FastSTM realtime hardware and the measurement and evaluation software have been adapted to our VT-STM and improved to allow routinely fast measurements. As shown in fig. 4, the setup could reveal the on surface polymerization of ethene with a time resolution of 4 images/s, thereby resolving the first dimerization step (results in **P7**) that would otherwise not be observable, since the dehydrogenation requires a critical temperature that cannot be underrun, while the resulting species is quite mobile. However, this imaging frequency is below the specifications since our sample holder, even if well suited for slow measurements, is not stiff enough to permit fast measurements without the occurrence of parasitic mechanical frequencies. While an improved sample holder has been developed in collaboration with W. Stiepany (MPI for Solid State Research, Stuttgart), we can state that our colleagues in Trieste have succeeded with the same FastSTM setup to reach imaging frequencies of 100 images/s (10 kHz fast scanning frequency). Hereby, they managed to reveal temperature-driven changes of the graphene edge structure on Ni(111) [6].

Fig. 4 FastSTM series of ethene polymerization. Observation of the PAH chain formation at 448 K, $p(\text{ethene})=8 \cdot 10^{-8}$ mbar. Image parameters: $I=1.0$ nA, $U=0.8$ V, 14×14 nm², acquisition of 4 images/s.



P9. FastSTM: How to tune the scan movement in a conventional microscope

Status: published and patented

Dri, Carlo; Esch, Friedrich; Africh, Cristina; Comelli, Giovanni: *How to select fast scanning frequencies for high-resolution fast STM measurements with a conventional microscope*. Measurement Science and Technology **23**, 2012, 055402.

Esch, Friedrich; Dri, Carlo; Comelli, Giovanni; Africh, Cristina; Spessot, Alessio: *A method for driving a scanning probe microscope at elevated scan frequencies*, European patents EP 2428804 A1 and B1 (issued 2012), US patents US8726409 and US20120066799 (issued 2014).

The implementation of fast measurement modes in conventional scanning tunneling microscopes (STM) generally implies that at least the fast scanning frequency reaches or exceeds the first resonance frequency of the scanning stage. We present a straightforward protocol for the determination of accessible frequency windows, where high spatial resolution can be routinely achieved and maintained during the fast scanning movement. This protocol relies on a simple, *in situ* method to

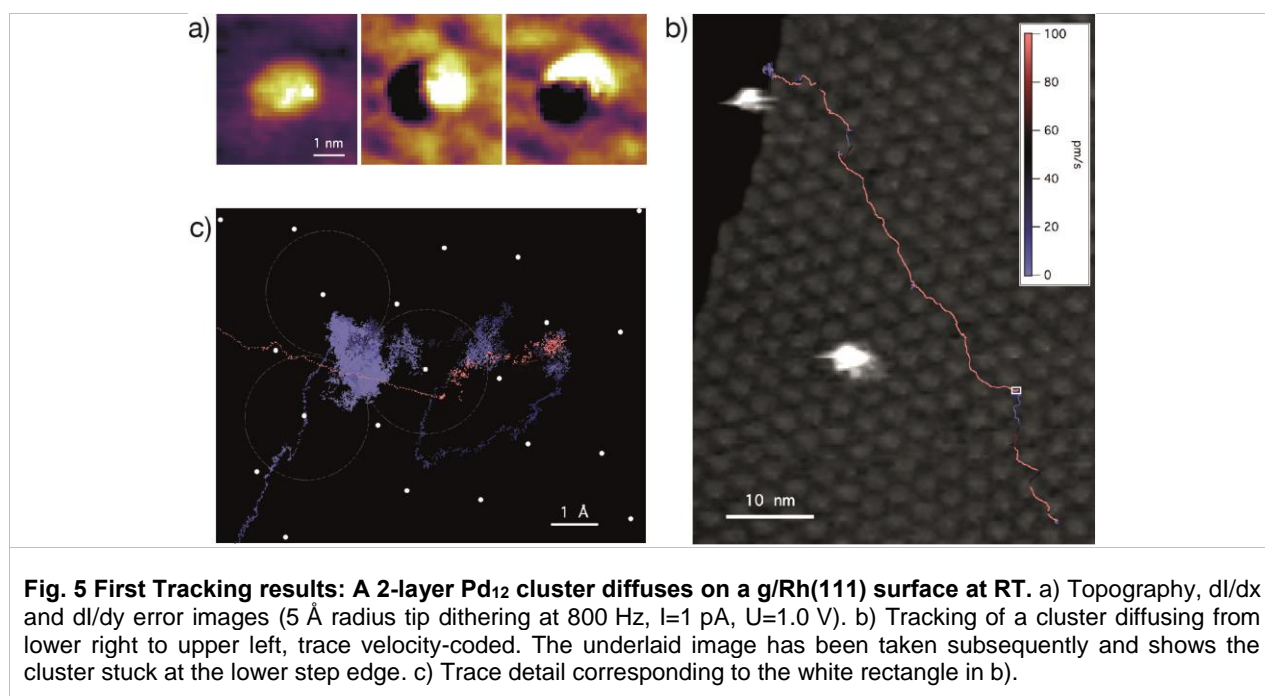
locate these frequency windows by measuring the response in the characteristic probe signal while varying the tip-sample distance and can also be applied to other types of scanning probe microscopes with sufficiently fast probe signal detection.

P10. Tracking: Implementation and first results

Status: implementation accomplished, ongoing research

For the realtime STM control module acquired in the first part of the project, an independent Tracking software has been developed and tested in the course of a PhD thesis, parallel to the FastSTM implementation. This software allows now for a seamless cluster tracking that starts upon tip relocation on a specific cluster (via mouse click in the commercial, slow STM control program). The cluster offset is then detected (via error signal dI/dx and dI/dy by software lock-in algorithm) and corrected for (PI algorithm), with a high temporal (10 ms) and spatial resolution (well below 1 Å). A dithering frequency of 800 Hz permits the use of slower, highly sensitive STM preamplifier amplification stages. Thus, the fast Tracking performances can be reached at **extremely mild scanning conditions**, with tunneling currents down to 1 pA.

Care has been taken to characterize the Tracking performance by registering error signal images (see fig. 5a) or by tracking test tip displacements (induced by the commercial, slow STM control program, not shown). A first measurement of the diffusion of a 2-layer-high Pd_{12} cluster on g/Rh(111) is shown in fig. 5b and demonstrates that the movement can be followed over long time ranges (≥ 30 min) and distances (up to 60 nm from starting point). The observed cluster trace points to anomalous superdiffusion, where long range diffusion sequences alternate with periods of quiescence. The high lateral and temporal resolution that can be reached is illustrated in fig. 5c, an enlargement of the white rectangle in fig. 5b. The cluster arrives from the lower left, resides for long time in a strong binding site and accelerates, once adjacent cells have been explored. As a guide to the eye, white dots indicate the graphene carbon atom mesh and the three shallow circles indicate the dimensions of the metal support atoms. The obtainable resolution is so high that we anticipate to be able to observe details on cluster slowing down and acceleration, on their coupling to cluster height changes and changes in the electronic structure (by parallel conductance measurements).



Measurement and evaluation software are now fully developed. Evidencing these phenomena and excluding tip effects requires, however, a much larger set of data, a demanding challenge for an experienced experimentalist as the PostDoc we apply for.

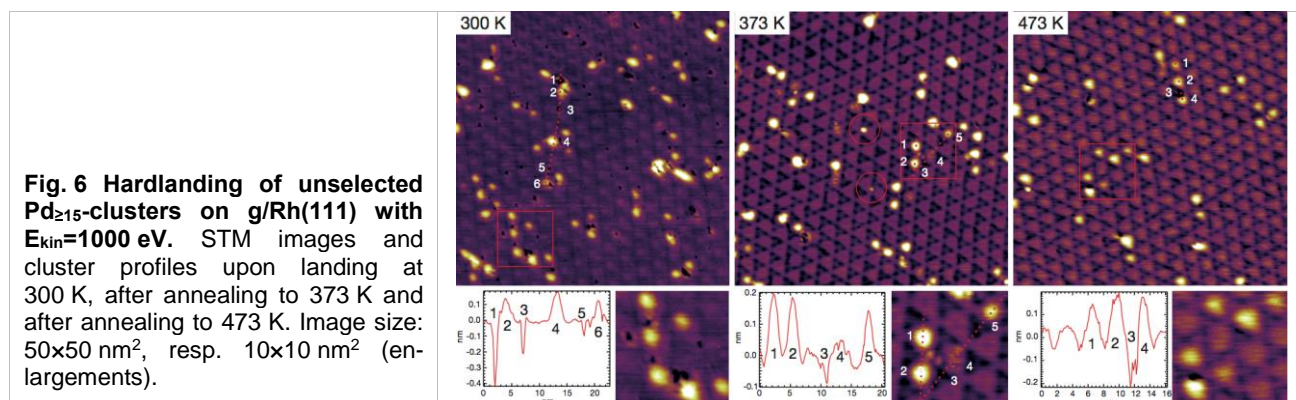
P11. Hard Landing: Creating clusters below a graphene membrane

Status: ongoing research

The size-selected cluster source offers the particular opportunity to control the kinetic energy of clusters upon deposition. While indeed Pd_{19} clusters **softland** at kinetic energies below 20 eV (they diffuse easily, can be manipulated by the tip and leave back an intact graphene film), they **fragment** above 50 eV and **get immobilized** in significant amounts above 100 eV, in agreement with the findings of the Palmer group for Ag cluster pinning on HOPG [7]. While the 2- to 3-layer high clusters are still bound to ring-hollow sites, as for soft-landing, the 1-layer high fragments bind at ring-top sites, indicating that they already penetrated the graphene film and intercalate at the sterically less confined sites below the film.

Defects in the graphene film can only be recognized upon much higher cluster impact energies. In fig. 6, the clusters have been landed with 1000 eV kinetic energy (at RT) and one observes several-Å deep holes of roughly 1 nm diameter that map the true cluster shape. The clusters that are shot through the graphene film and form craters with characteristic shapes that can also be formed upon sputtering (see extensive studies by Michely and coworkers, [8]). These shapes are multiple protrusions and rings, whereby the volume increases with cluster size and deposition energy.

At these high impact energies, almost all clusters penetrate the graphene film. Upon annealing, the graphene film defects in graphene migrate to those surface sites that are strongly interacting with the substrate, while the protrusions below the carbon film order below ring-top sites, where they are stable against further annealing. Interestingly, below some ring-top sites small, highly diffusive clusters remain encapsulated. This opens the possibility to study their confined diffusion below a graphene-Moiré tent with our fast detection methods - a perfect system for studying the interaction potential by an ergodic analysis.



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